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Recent Developments in Catalyst-Related PEM Fuel Cell Durability

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Abstract:

Cost and durability remain the two major barriers to widespread commercialization of polymer electrolyte membrane fuel cell (PEMFC)-based power systems. While a number of commercial Pt-based alloy cathode catalysts exceed the beginning-of-life (BOL) targets, these activities, and the overall cathode performance, degrade via a variety of mechanisms described herein. The design and development of active and robust materials and eliminating the need for vehicle mitigation strategies would greatly simplify the operating system, allowing for greater transient operation, avoiding large hybridization and curtailing of fuel cell power. Although system mitigation strategies have provided the near-term pathway for FCEV commercialization, material-specific solutions are required to further reduce costs and improve operability and efficiency. Future material developments should focus on stabilization of the electrode structure and minimization of the catalyst particle susceptibility to dissolution from oxide formation and reduction over PEMFC cathode-relevant operating potentials plus minimization of support corrosion.

Abstract:

Cost and durability remain the two major barriers to widespread commercialization of polymer electrolyte membrane fuel cell (PEMFC)-based power systems, especially for the most impactful but challenging fuel cell electric vehicle (FCEV) application. Commercial FCEVs are now on the road; however, their PEMFC systems do not meet the cost targets established by the U.S. Department of Energy, primarily due to the high platinum loading needed on the cathode to achieve the requisite performance and lifetime. While the activities of a number of commercial Pt-based alloy cathode catalysts exceed the beginning-of-life (BOL) targets, these activities, and the overall cathode performance, degrade via a variety of mechanisms described herein. Degradation is mitigated in current FCEVs by utilizing a cathode catalyst with a lower BOL activity (e.g., much lower transition metal alloy content and larger BOL nanoparticle size), necessitating higher catalyst loadings, and through the utilization of system controls that avoid conditions known to exacerbate

degradation processes, such as limiting the fuel cell stack voltage range. The design and development of active and robust materials and eliminating the need for vehicle mitigation strategies would greatly simplify the operating system, allowing for greater transient operation, avoiding large hybridization and curtailing of fuel cell power. Although system mitigation strategies have provided the near-term pathway for FCEV commercialization, material-specific solutions are required to further reduce costs and improve operability and efficiency. Future material developments should focus on stabilization of the electrode structure and minimization of the catalyst particle susceptibility to dissolution from oxide formation and reduction over PEMFC cathode-relevant operating potentials plus minimization of support corrosion. *Ex situ* accelerated stress tests have provided insight into the processes responsible for material and performance degradation and will continue to provide useful information on the relative stability of materials and benchmarks for robust and stable materials-based solutions not requiring system mitigation strategies to achieve adequate lifetime.

Introduction

The past decade has seen tremendous progress in understanding and addressing the underlying phenomena responsible for voltage losses and performance degradation of polymer electrolyte membrane fuel cells (PEMFCs). Cost and durability, however, continue to be the two major barriers to widespread implementation of PEMFC-based power systems. These barriers are intimately linked because the costly Pt catalyst is also the major source of PEMFC performance degradation.[1] Fuel cell electric vehicles (FCEVs) are in the early stages of commercialization, with approximately 7,000 FCEVs sold in the United States thus far.[2] The cost of the PEMFC components in these stacks, however, do not meet the long-term cost targets set by funding organizations, such as the U.S. Department of Energy (DOE).[3] For example, the Toyota Mirai PEMFC system is projected to cost $233/kW at 1,000 stacks/year volume manufacturing,[3] while the U.S. DOE has targeted a system cost of $30/kW by 2025.[3] Therefore, although substantial progress has been made in PEMFC materials and system development, research and development (R&D) in the area of PEMFC performance and durability remain a top priority.

In 2015, the U.S. DOE Fuel Cell Technologies Office (FCTO) formed the Fuel Cell Performance and Durability Consortium (FC-PAD), a multidisciplinary team comprised of five national laboratories focused on enhancing the performance and durability of PEMFCs to meet the U.S. DOE transportation cost targets. As thrust coordinators of FC-PAD, we present here a review of recent progress in our fundamental understanding of membrane-electrode assembly (MEA) and catalyst durability, concentrating on results from 2018 to the present.

Ex Situ Stability of Pt-based PEMFC Cathode Electrocatalysts

Platinum-based electrocatalysts are currently used in PEMFCs due to their high oxygen reduction reaction (ORR) activity and relatively high stability in the acidic and oxidizing environment of the PEMFC cathode. The U.S. DOE has set a target for ORR mass activity (MA) of >0.44 A/mg$_{PGM}$@0.9 V$_{iR\text{-}free}$ in a PEMFC MEA.[4] Several commercial and experimental Pt-based electrocatalysts meet or exceed this target at beginning of life (BOL).[5,6] Due to the complexity of the MEA structure, *ex situ* methods utilizing aqueous acidic electrolytes, such as rotating disk electrode (RDE), are often employed to determine a catalyst's intrinsic activity and to glean a fundamental understanding of degradation mechanisms.[7-9] These measurements have been coupled with additional analysis, *e.g.* inductively coupled plasma-mass spectrometry (ICP-MS, batch method or on-line)[10-14] and analysis of the evolved gases using

electrochemical mass spectrometry [15-18] to evaluate catalyst stability as a function of various stressors (*e.g.* potential, temperature, and relative humidity). Such studies have elucidated the dependence of Pt dissolution rates on cathode catalyst potential and potential cycling.[e.g., 17, 18] These measurements show that Pt dissolution increases exponentially with increasing steady-state potential or upper limit of potential cycling above ~0.85 V [17, 18, 19] (Figure 1a,b).[18]   It was found that Pt re-deposition competes with dissolution, greatly affecting the net amount of dissolved Pt (Figure 1c).[17] The Pt dissolution rate is a function of the particle size; the dissolution rate of 1-2 nm diameter Pt nanoparticles is over 20x that of 5 nm Pt particles.[20] Cathode catalyst layers (CCLs) in commercial PEMFC utilize PtCo alloys due to their enhanced ORR MA versus Pt.[21-25] Alloys can introduce additional durability challenges associated with dissolution of the transition metal (TM) from the alloy (e.g., TM=Co, Ni, Fe, Cr). Recent measurements show a potential dependence of Pt and Co dissolution rates in triangle potential sweeps, with higher Pt dissolution rates during the cathodic vs anodic scans to high potentials and Co dissolution at all potentials relevant to the PEMFC cathode.[19]

Catalyst Degradation in Operating MEAs

While RDE is the most widely used technique for screening the electrochemical activity of catalysts, the more relevant metrics are performance and durability assessed in operating PEMFC MEAs. Catalyst durability protocols comprised of potential cycling with intermittent performance testing and diagnostics, termed accelerated stress tests (ASTs), are often used for the rapid evaluation of catalyst and support durability.[4, 26-27] A primary catalyst degradation mechanism observed during ASTs is the loss of nanoparticle electrochemically-active surface area (ECSA) due to particle growth arising from a combination of coalescence and dissolution/reprecipitation mechanisms.[28,29] Nanoparticle growth is dependent on a number of factors, including catalyst physicochemical properties such as BOL particle size, shape, composition, support properties and interactions, interparticle spacing, pore size distribution,[29] and location of particles on the support, as well as operating conditions such as potential, potential sweep rate, upper/lower potential limit (UPL, LPL) of the sweep, temperature, and relative humidity (RH). [26,30,31] Modeling of Pt dissolution data acquired from ASTs of MEAs indicates that the total amount of Pt that dissolves reductively as PtOx during the cathodic scan far exceeds the amount that dissolves oxidatively as Pt and PtOH during the anodic scan (Figure 1c).[33] Measurements also show that the amount of leached Co is a strong function of UPL and is less impacted by the LPL.[31] Other studies found that the width of the particle-size distribution (PSD) is the determining factor dictating ECSA stability: Pt nanoparticles supported on high surface area carbon (HSC) with initial particle sizes of 2, 3, and 4 nm and narrow PSD standard deviations ($\sigma_d < 10\%$) exhibited degradation independent of the particle size over the entire AST duration and changes in MA were found to be approximately proportional to ECSA losses.[33] In this case, Pt nanoparticles as small as 2 nm were found to be durable, maintaining the highest MA.[33] It has also been demonstrated that the UPL has a large effect on the Pt particle oxidation and that lowering the UPL can greatly increase the catalyst durability.[4, 34-36] RH has a strong effect on both ECSA degradation and the corresponding loss in H_2-air performance. Electrode degradation, as characterized by losses in ECSA and MA, is more severe under wetter conditions (100% RH) than drier conditions (40% RH). Although difficult to infer definitively from experiments with two parameters varying simultaneously, the observed losses in ECSA, MA, and cell voltage are more severe at higher cell temperatures (95°C vs. 55°C).[37-39]
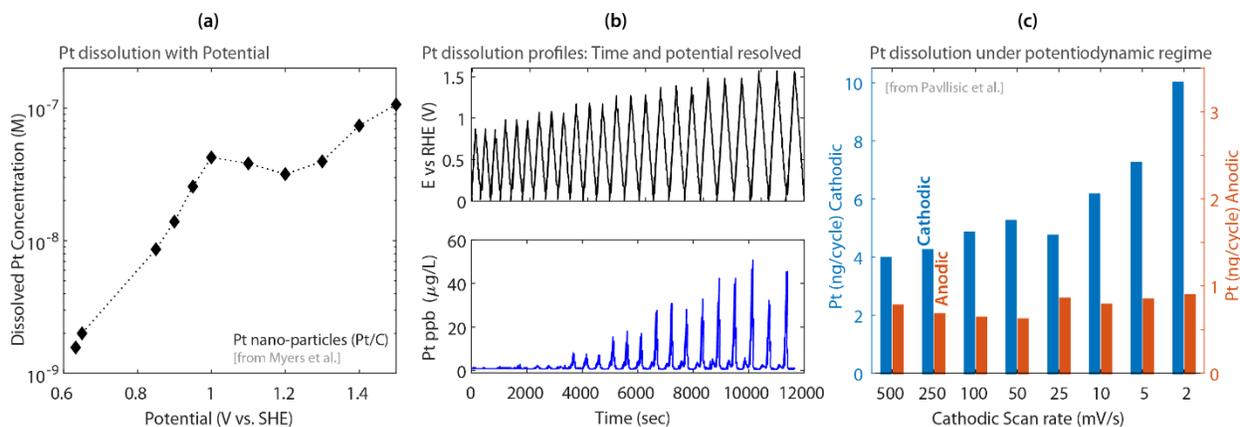
Figure 1 (a) Steady-state concentration of dissolved Pt as a function of potential for Pt nano-particles (Pt/C) [18] (b) Pt dissolution profiles: time and potential-resolved dissolution profiles of 3 nm Pt catalyst (experimental conditions: 0.1 M HClO$_4$, potential window: 0.05 to different UPL (0.9–1.6 V), scan rate 5 mV/s).[data from ref 17] (c) Amounts of Pt dissolution for cathodic and anodic portions of potential cycle as a function of cathodic scan rate (potential window: 0.05 to 1.6V). [17]

In addition to ECSA loss as a primary degradation mechanism, Pt-TM alloy nanoparticle catalysts show a large degree of TM leaching after ASTs and simulated vehicle drive cycles.[27] Interestingly, it was recently reported that dissolution-related degradation could be mitigated by limiting the lowest potential experienced by a Pt-alloy catalyst to values higher than those needed for full reduction of Pt oxide.[30] These results from MEA studies appear consistent with aqueous cell results where Co dissolution was independent of lower potential > 0.70V. As shown in Fig. 2a, subjecting an MEA with a 4.5 nm PtCo alloy cathode catalyst to simulated drive cycles (75,000 cycles over 1200 hours) resulted in substantially higher cathode catalyst particle growth (7.4 nm) than observed after 30,000 cycles of the standard AST protocols (5.0 and 5.1 nm).[26] The small- and intermediate-sized PtCo particles, which are typically Pt-rich in the as-received condition, undergo minimal change in composition. Nanoparticles with higher Co content, however, dramatically decrease in number over the course of the ASTs.[26,27] Intermediate- and larger-sized PtCo nanoparticles, with a higher Co content, can transform into hollowed-out shells driven by continuous leaching of Co from the PtCo catalysts (Figure 2b).[27] This loss of Co from the catalyst particles results in particles with higher Pt content and correspondingly lower ORR MA as the compressive strain of the lattice induced by the smaller Co atoms is lost (Figure 2c).[26-27,30,39] Additionally, advanced Pt-alloy catalysts demonstrate higher local O$_2$ transport resistance at high current densities and lower catalyst loadings than Pt catalysts, which can most likely be attributed to the higher current per unit of catalyst surface area due to the lower initial ECSA at BOL and TM leaching into the ionomer.[26,31,41] Significant performance losses at high current density, associated with local O$_2$ transport, have been observed at EOL with advanced Pt-alloy catalyts due to to these morphological changes and resulting loss of ECSA with cycling and transition metal leaching into the ionomer.[33] TM cations have been shown to affect ionomer water uptake which in turn affects ionomer conductivity and oxygen permeability, especially under low relative humidity conditions.[6,33,40,41]
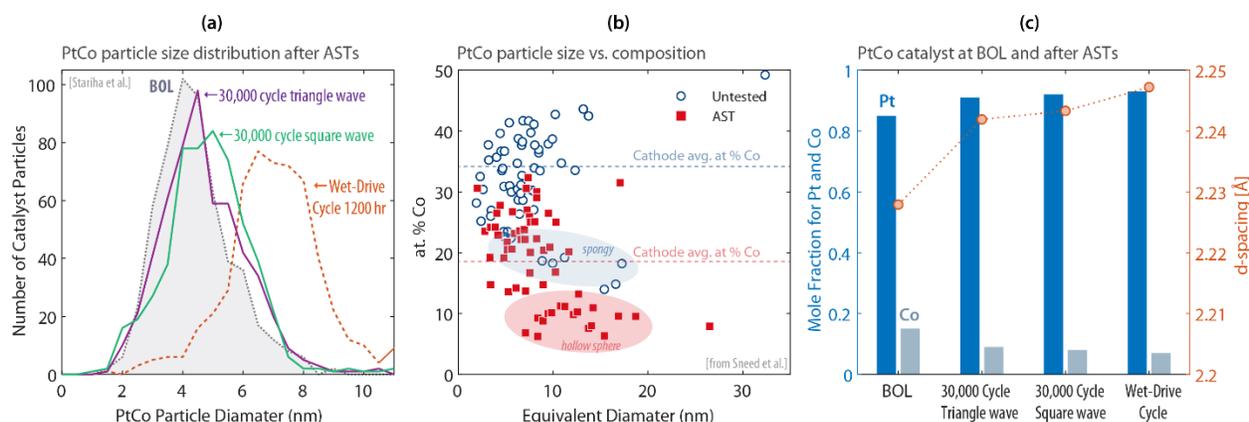
Figure 2 (a) PtCo particle size distribution at BOL, after 30,000 cycles catalyst ASTs (for square-wave and triangle-wave), and after a 1200 hour wet drive cycle.[26] (b) PtCo particle size vs. composition for individual particles in BOL and EOL MEAs. Bulk CCL compositional averages shown by dashed lines for BOL (blue) and EOL MEAs (red). Transparent ellipses denote size vs. composition regimes where BOL spongy nanoparticles (blue) and EOL hollow sphere nanoparticles (red) were observed [27]. (c) Relative Pt and Co concentration and the d-spacing for a PtCo catalyst at BOL and after 30,000 hr-ASTs (with square- and triangle-wave) and after wet drive cycle testing at 100% RH [adapted from ref 42].

Durability of Commercial Materials and Relationship with Vehicle Mitigation Strategies

The commercialization of passenger FCEVs provides an opportunity to baseline the durability of road-worthy commercial materials. Cells from two Toyota Mirai FCEVs (after 300 and 3000 hr of real-world driving) were provided to FC-PAD for detailed characterization using the broad range of analytical techniques available within FC-PAD to help detail state-of-the-art commercial materials to guide future material developments.[23,42,43,44] Little difference in the structure of materials comprising the CCL was observed with respect to real-life operation time (e.g., 300 vs. 3000 hr): the PtCo cathode catalyst nanoparticle size was nearly identical at 4.7 nm (Figure 3a) and 4.8 nm (Figure 3b) after 300 and 3000 hr drive time (Figure 3d), respectively, by transmission electron microscopy (TEM) and 4.86 nm and 4.96 nm by small-angle X-ray scattering (SAXS). However, after subjecting the cells to the U.S. DOE-Fuel Cell Technical Team (FCTT)-recommended catalyst and support ASTs, the PtCo particle size increased substantially to 6.7 (Figure 3c) and 5.3 nm, respectively, and thus the cathode catalyst did not pass the U.S. DOE durability target of <40% ECSA loss after 30,000 cycles. Characterization also demonstrated that while the Co content of the PtCo alloy nanoparticles was essentially unchanged after 3,000 hrs of driving, the ASTs caused substantial preferential loss of Co from the cathode catalyst particles. It is evident that the system mitigation strategies employed in the Toyota Mirai (e.g., limiting cell voltage during idling [45]) were successful in preventing the majority of component degradation, albeit at higher catalyst loadings than the U.S. DOE targets (0.37 mg_{Pt}/cm^2 vs. 0.125 mg_{Pt}/cm^2). While these system mitigation strategies prevent catalyst degradation, they incur additional costs for added valves and controls and limit the fuel cell operating power window (i.e., turndown voltages).[46]
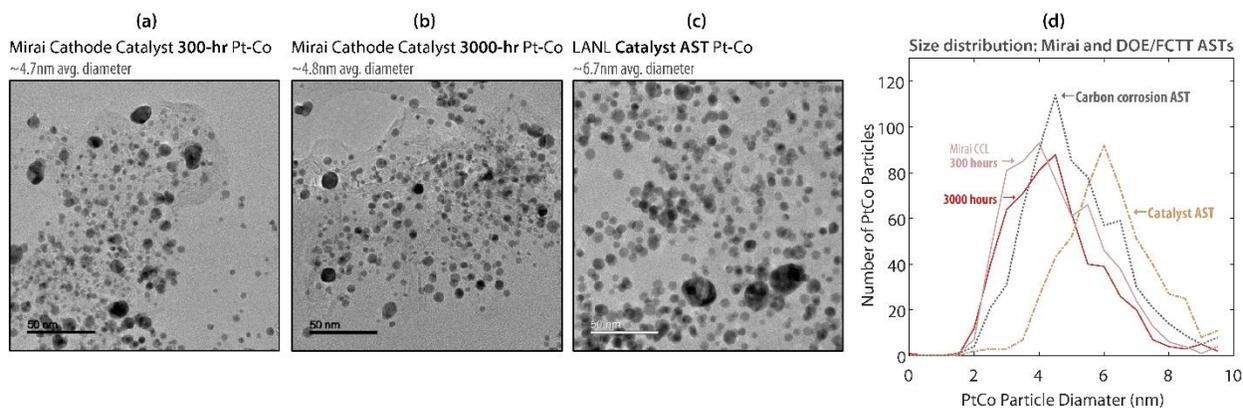
Figure 3 TEM images of the Toyota Mirai cathode catalyst after operation for (a) 300 hr and (b) 3000 hrs, and (c) after 30,000 catalyst AST cycles [adapted from ref 23] (d) PtCo PSDs for the cathode catalyst operated for 300 hr and 3000 hr and after application of the U.S. DOE/FCTT-recommended catalyst and carbon corrosion ASTs [23].

Catalyst-Layer Degradation and Carbon Support Corrosion

Another primary degradation mode is related to structural changes of the CCL, including changes to the secondary pore network, ionomer, and carbon-support particle/agglomerate distribution.[47, 48] Carbon corrosion or oxidation of the carbonaceous support, in particular, leads to a large increase in oxygen transport resistance.[49] A strong catalytic effect of Pt on the carbon-corrosion rate was observed;[48] although the carbon-corrosion rate depends only on the amount of Pt and not on the catalyst composition (*i.e.*, Pt or Pt-alloy).[47] Carbon corrosion has typically been associated with high potential excursions, such as those occurring during start-stop operation;[50] however, it has been found that corrosion occurs at both high potentials (> 1.2V) and, to a minor extent, at low potentials and is accelerated by rapid changes in potential.[47,48] Modeling analysis correlated increased mass transport limitations after ASTs to changes in the local oxygen transport resistance to the catalyst particles.[47] High surface area carbon (HSAC) supported catalysts show a rapid decrease in ECSA and MA during the carbon corrosion AST, whereas the MA of Pt catalysts on low-surface area carbon, albeit initially much lower, remains almost unchanged.[47] In addition, supports with a high surface density of graphene sheet edges have been shown to be prone to oxidation and be more susceptible to carbon corrosion.[51]

The two recommended ASTs described herein are intended to separately/independently probe the stability of the electrocatalysts and carbon supports. It is possible to predict the performance of a degraded sample simply by measuring or modeling the ECSA over the lifetime of the MEA, as long as carbon corrosion is avoided. However, electrodes subjected to both the catalyst and the support ASTs show significant thinning. An SEM cross-section of the 300 hr operated Toyota Mirai cathode catalyst layer was measured to be 10-11 micron in thickness (Figure 4a), however after the catalyst AST (0.6 to 0.95 V) it exhibited thinning (Figure 4b) to 8-9 microns.[23] The catalyst support AST caused substantially more thinning and compaction of the electrode to approximately 4 micron (Figure 4c), resulting in a dramatic loss in electrode porosity.[23]

Recent *operando* X-ray computed tomography (XCT) studies of an electrode layer during ASTs illustrate that the CCL undergoes substantial changes in porosity during cycling with an increase in higher porosity during the first stage of cycling and a shift to decreases in porosity during more advanced stages of cycling.[52] Post-AST FIB-SEM analysis has shown samples exhibit a shift in pore-size distribution to larger pores, however the overall porosity of the cathode remains unchanged (Figure 4d). While performing

the ASTs at higher cell temperatures results in a thinner cathode, there were no obvious differences in the CL pore structure in the cells cycled at higher temperatures versus those cycled at 80°C.[49]

In addition to performance degradation resulting from potential driven processes of catalyst particle growth, loss of transition metal, and carbon corrosion, other degradation processes are driven by the changing environment within the CL. For example, wet/dry cycling of an MEA, resulting in water intrusion and evaporation processes in the CL, leads to considerable growth of the CL agglomerates and to the formation of pinholes and cracks (see Figure 4e fresh and 4f after water intrusion cycles).[53] These morphological changes of the CCL such as crack formation and propagation were imaged during catalyst ASTs by XCT and included catalyst layer movement which increases as the CL degrades, and was also attributed to porosity change and CL flooding.[52] Ohmic resistance is also slightly increased after the water intrusion.[53] Ionomer degradation and thinning in the CLs has also been attributed to potential cycling.[54-55] While the materials and conditions have been found to be crucial to the rates and mechanisms of PEMFC performance degradation, MEA fabrication methods have not (e.g., with and without hot-pressing of the electrodes to the membrane).[56] Moreover CCL thickness was noted to be reduced after simulated drive-cycle operation, not due solely to carbon corrosion, although carbon corrosion played a role, as witnessed by the compaction of the material in the catalyst layer leading to decreased porosity and increased mass-transport limitations.[47] Cracks in the electrode layer have also been demonstrated to affect the performance and durability of PEMFCs. While recent studies have demonstrated that deliberate cracking of the electrode layer can result in improved water management and better fuel cell performance,[57] it has been established that membrane failure via cracking under mechanical stress (RH cycling) is exacerbated by the presence of electrode cracks.[58] These results indicate that in addition to the catalyst, support and ionomer durability; electrode layer morphology plays an important part in the performance and durability of fuel cells.

(a) Cell SEM cross-section: After 300 h of driving
(b) After 300 h of driving + 30,000 catalyst ASTs
(c) After 300 h of driving + 30,000 support ASTs
(d) Pore-size distribution: 3D reconstruction of FIB-SEM images
(e) Catalyst layer surface - Fresh
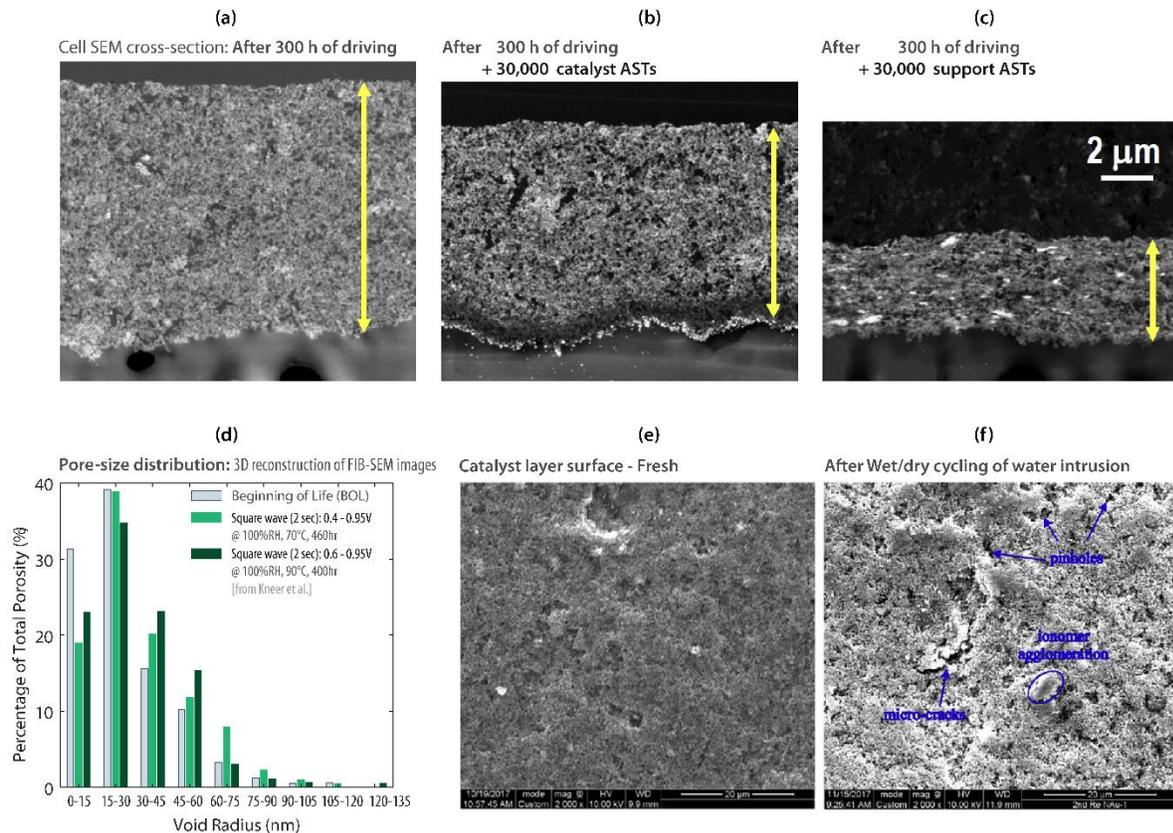(f) After Wet/dry cycling of water intrusion

Figure 4 SEM cross-section images of cells from a Toyota Mirai after (a) 300 h of driving, (b) 300 h of driving + 30,000 catalyst ASTs, and (c) 300 h of driving + 30,000 support ASTs,[23] (b) Pore size distribution extracted from 3D reconstruction of FIB-SEM images of fresh and AST-cycled cells.[49] SEM micrographs of a catalyst layer surface (e) in fresh state, and (f) after wet/dry cycling of water intrusion. (SEM images reproduced from ref 53).

Summary

Degradation of Pt and Pt-alloy catalyst nanoparticles and the cathode electrode structure continues to be major concerns for hindering the commercialization of PEMFCs for transportation applications. Currently-used PtCo catalysts have stability issues arising from ECSA loss due to particle growth and transition metal leaching. Methods to alleviate these issues have been identified and include BOL catalysts with lower Co content (~ 10% Co), mono-disperse nanoparticle distributions, and larger BOL catalyst nanoparticle sizes of 4-5 nm. However, such methods limit the catalysts' ORR mass activity due to the minimal lattice strain induced by relatively low amounts of Co and low mass-specific surface area (m^2/g_{Pt}) of larger particles, thereby necessitating higher Pt loadings to achieve performance targets. Many of the primary degradation mechanisms can be mitigated by implementing system operating strategies, as is the case for systems in current commercialized FCEVs. Although system mitigation strategies have provided a near-term pathway for commercialization, material-based solutions would help to reduce cost and improve operability and efficiency. Future material R&D should focus on stabilization of the electrode structure and minimization of the susceptibility of catalyst nanoparticles to dissolution from oxide formation and reduction over PEMFC cathode-relevant potentials plus minimization of support corrosion.

Materials that can be employed to avoid the vehicle mitigation strategies, such as limiting the operating voltage range of fuel- cell systems, would simplify the operating system and allow for greater transient operation. This would avoid large hybridization and curtailing of fuel cell power during times of extended vehicle idling. Catalyst and support ASTs will continue to provide useful information on the relative stability of materials and benchmarks for robust and stable materials-based solutions not requiring system mitigation strategies to achieve adequate lifetime.

Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Acknowledgements

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　　* of special interest
　　** of outstanding interest

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　　The authors review the current Precious Group Metal (PGM) and PGM-free literature and provide a perspective on advanced electrocatalysts for PEMFCs. They conclude that ordered PtM intermetallic nanostructures hold promise for both enhanced performance and durability while the degree of graphitization of the carbon and its pore structure can enhance these further. They also indicate that transition metal and nitrogen co-doped carbons (M-N-C) can be promising for this application if their durability at > 0.6V is improved. They finally illustrate the importance of electrodes with robust three-phase interfaces in making effective use of advance electrocatalysts.

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